

Side-Chain Crystallinity. IV. Mechanical Properties and Transition Temperatures of Copolymers of Methyl Methacrylate with Higher *n*-Alkyl Acrylates and *N*-*n*-Alkylacrylamides

Synopsis

Mechanical properties were correlated with glass transition temperatures for a series of random copolymers of methyl methacrylate with comonomers selected from the higher *n*-alkyl acrylates and *N*-*n*-alkylacrylamides. The plasticizing comonomers were the *n*-butyl, 2-ethylhexyl, *n*-octadecyl, and oleyl acrylates, and the *N*-*n*-butyl-, *N*-*n*-octyl-, *N*-*n*-octadecyl-, and *N*-oleylacrylamides. The complete range of compositions was investigated. However, the bulk of the data was obtained on compositions in the glassy region below the onset of the vitreous transition. In this region it was found that the decrease in tensile and flexural moduli and strengths with increase in internal plasticizer for all of the systems was directly proportional to the decrease in T_g . It was concluded that the additive contribution to the free volume made by each side-chain methylene group was alone responsible for the magnitude of the rate of change of properties. However, polar contributions of the amide group to stiffening the main chain exceeded those of the ester, so that the amides were less efficient plasticizers. An empirical equation was derived which described, with fair accuracy, the decrease in the mechanical parameters with composition for the amorphous copolymers. It was reasonably successful in predicting properties even into the composition range where the ambient testing temperature corresponded to or exceeded the transition temperature. In this transition region an accelerated decrease in the magnitude of the physical properties was observed. All samples exhibited brittle fracture except those tested in the transition region. Here the strain was largely irrecoverable flow. Side-chain crystallinity did not interfere significantly with the mechanical properties because moduli and strengths had already decayed to small values near the compositions where crystallinity commenced. Non-random copolymers of vinyl stearate and methyl methacrylate showed no internal plasticization, apparently because of macrophase aggregation.

INTRODUCTION

Few studies have been reported on the mechanical properties of plasticized polymers tested below their glass transition temperature T_g . This is probably because most plasticized compositions have technological im-

portance only above T_g .¹ Of the externally plasticized systems tested above T_g , cellulose esters and poly(vinyl chloride) have received the most attention,²⁻⁶ but some investigators studied even more crystalline polymers such as poly(vinylidene chloride)⁷ and polyethylene.⁸ In contrast, the plasticization of amorphous polymers, such as polystyrene⁹ and poly(methyl methacrylate),¹⁰ has received little attention because of the concomitant impairment of their mechanical properties. Crystallites extend the relaxation times associated with the rubbery response to deformation,^{5,11,12} thus opposing the effect of reduced chain entanglements caused by dilution by plasticizer.^{13a} Although some data on mechanical properties below the glass transition were included in reports dealing mostly with properties above T_g ,^{2,14} the only intensive study of a plasticized homopolymer in the glassy region was made by Boyer.⁹ His data showed a precipitous drop in the tensile strength of polystyrene, proportional to the decrease in glass temperature, throughout the region. He attributed this decline to weaknesses generated by end groups contributed by the plasticizer to the polymer matrix.¹⁵

Limited data on internally plasticized systems demonstrated much the same type of behavior. Moduli and tensile strengths decreased steadily as the flex temperature T_f decreased, even in the composition range where T_f was above room temperature. The trend was followed by poly(vinyl chloride) copolymerized with the long-side-chain esters,¹⁶ and by polyacrylonitrile modified with higher *n*-alkyl acrylates¹⁷ and *N*-*n*-alkylacrylamides.¹⁸ Interpretation of these data is made difficult, however, by the limited range of composition studied, the influence of strongly polar groups on conformational freedom in the main chain, and the uncertainty presented by the use of the flex temperature instead of the glass temperature when the modulus-temperature curves are broad.¹⁸⁻²⁰ Further difficulties have resulted from ignorance of the degree and effect of main-chain and side-chain crystallinity. However, knowledge gained from recent studies of the thermodynamics of the crystallinity present in the side chains of homopolymers of the higher *n*-alkyl acrylates, *N*-*n*-alkylacrylamides, and vinyl esters,²¹ together with extensive data on crystallinity in copolymers of *n*-octadecyl acrylate with amorphous comonomers,²² and the influence of this crystallinity on T_g ,²³ was expected to be useful in interpreting results from the mechanical property data collected in this investigation.

In this investigation some mechanical properties are presented on copolymers of selected *n*-alkyl acrylates and *N*-*n*-alkylacrylamides with methyl methacrylate over the composition range. Consequently mechanical properties were obtained both below and through the transition region. The *n*-butyl, *n*-octyl (or 2-ethylhexyl), *n*-octadecyl, and oleyl derivatives of the two classes of monomers were selected to permit a study of the effect of a wide range of side-chain lengths. By contrasting the influence of crystalline *n*-octadecyl with amorphous oleyl side chains, the effect of side-chain crystallinity on the mechanical properties could be separately isolated. Mechanical properties were correlated with the glass

transition temperatures, and the contribution of each added methylene group in the side chains to the physical properties was approximated. Methyl methacrylate, whose homopolymer is amorphous and has a high glass transition temperature, was selected as a monomer which would yield generally random copolymers with these comonomers. However, some drift in composition with conversion could be expected.²⁴ Finally one nonrandom system (vinyl stearate-methyl methacrylate) and one terpolymer acrylate system were included for comparison with the bulk of the data.

EXPERIMENTAL

n-Alkyl Acrylates and *N*-*n*-Alkylacrylamides

The ethyl, *n*-butyl and 2-ethylhexyl acrylates were from commercial sources. They were washed free of inhibitor with aqueous alkali and dried prior to polymerization. The preparations of *n*-octadecyl acrylate²¹ and oleyl acrylate²² as well as *N*-*n*-octadecylacrylamide,¹⁸ *N*-oleylacrylamide,²⁵ *N*-*n*-octylacrylamide,¹⁸ and *N*-*n*-butylacrylamide¹⁸ were described. The vinyl stearate was that described previously.²¹

Polymerization Procedure

The preparation of the *n*-octadecyl acrylate or vinyl stearate copolymers of methyl methacrylate has been described.²² The remaining comonomers were polymerized in sealed bottles under nitrogen in benzene (4 mole/mole of total monomer, except oleyl acrylate, *N*-*n*-octadecyl- and *N*-oleylacrylamide, 1 mole/mole of total monomer) at 60°C with the use of 0.2 mole-% of azo bis isobutyronitrile as initiator, for 72 hr, except for the *N*-*n*-octadecylacrylamide, for which a temperature of 80°C was employed. All of the polymers were isolated in methanol (5 ml/g) at room temperature and freed of monomers by repeated extractions with refluxing methanol (5 ml/g). Copolymers soluble in methanol (certain *N*-*n*-butyl and *N*-*n*-octylacrylamide compositions) were extracted with petroleum ether. The polymers were dried in thin layers. Yields were between 84% and 98%, and the copolymer or terpolymer composition, calculated from elemental analysis, agreed with the feed composition within experimental error. Consequently correlations of data in this paper were made against feed compositions to decrease experimental scatter.

Osmometric molecular weights were determined by reported procedures,¹⁸ except that single determinations were done for each sample. The degrees of polymerization, calculated from weighted comonomer molecular weights using the feed compositions, are listed in Table I for some of the copolymers. Degrees of polymerization for the balance can be found in previous papers from this laboratory.^{22,23} Most of the degrees of polymerization listed in Table I are high enough to indicate only slight depression of the glass transition and mechanical properties by chain-end effect.⁹

TABLE I
Degrees of Polymerization of Copolymers^a

Feed composition, mole fraction ^b	Degrees of polymerization ^c						
	BA	EHA	BAM	OCAM	OAM	OLAM	OA + EA
0.050	750	830	890	900	1200	1600	660
0.075	730	840	1000	970	1300	1500	610
0.100	860	920	610	1100	1100	1600	460
0.125	900	850	1300	1200	1100	1600	430
0.150	850	860	620	650	1200	1500	410
0.200	910	810	650	700	340	1300	550
0.300	980	540	780	730	330	840	680
0.400	960	470	—	—	330	660	560
0.500	1100	430	—	850	330	560	470
0.600	1300	410	—	900	370	360	460
0.750	1300	380	—	1000	350	290	464

^a Degrees of polymerization for copolymers of *n*-octadecyl acrylate,²² vinyl stearate,²² and oleyl acrylate with methyl methacrylate²³ were reported previously.

^b Compositions by elemental analysis agreed with these within experimental error.

^c Calculated by using a weighted average of the molecular weight of each comonomer. Designations are: BA, *n*-butyl acrylate; EHA, 2-ethylhexyl acrylate; BAM, *N*-*n*-butylacrylamide; OCAM, *N*-*n*-octylacrylamide; OAM, *N*-*n*-octadecylacrylamide; OLAM, *N*-*n*-oleylacrylamide; OA + EA, *n*-octadecyl acrylate + ethyl acrylate (terpolymer). The other comonomer copolymerized with all those listed in the table was methyl methacrylate.

Mechanical Properties

The procedures of Jordan et al.^{18,25} were followed. Tensile tests were run according to ASTM D882. The tests were made at 23°C and 50% RH.

Calorimetric Procedure

The operation of the differential scanning calorimeter has been described for the determination of side-chain crystallinity^{21,22} and the glass transition temperature.²³ All calculations and mathematical correlations were made with an IBM 1130 computer.

RESULTS AND DISCUSSION

General Features

The mechanical properties, per cent elongations, glass transition temperatures T_g , and flex temperatures T_f for all of the copolymers and terpolymers are listed in Table II. Discussion of the nonrandom copolymers (vinyl stearate-methyl methacrylate) and the terpolymers will be reserved for the end of the paper. The discussion immediately following, limited to random copolymers, includes the first eight copolymer series in Table II. The moduli and strengths generally decreased steadily as the proportion of the

long-side-chain comonomer increased. The decreases occurred to varying extents in the different copolymers even in that composition range, corresponding to the glassy region, where T_g was above room temperature. Increased rate of decrease of a property occurred at the concentration of plasticizing co-unit at which T_g was depressed below room temperature. In the glassy region, per cent elongations were generally small, and the ultimate strengths were characterized by brittle fracture.²⁶ Necking rupture²⁶ was never found. However, in the transition region, where some fractures were characterized by uniform extension,²⁶ the strain often showed irrecoverable flow. This accounted for some of the larger extensions found in the transition region and listed in Table II. The behavior here was similar to that of externally plasticized polystyrene,⁹ as long as the internally plasticized compositions were being tested in the glassy state below T_g . When side-chain crystallinity was present (as in the *n*-octadecyl acrylate and *N*-*n*-octadecylacrylamide copolymers), brittle fracture and small strains continued to occur through the transition region, as crystallite concentration increased. However, at the composition at which crystallinity commenced, the mechanical properties had already been reduced to impractically low values. In contrast, when the C_{18} comonomer was oleyl, ductile fractures and greater elongations characterized the ultimate strengths in the range of compositions corresponding to the transition region.

Effect of Side-Chain Crystallization on the Glass Transition Temperature

A linear decrease in the glass transition with increase in the weight fraction of fatty component was observed over the complete range of composition for all of the amorphous copolymers. However, with the crystallizing comonomers, *n*-octadecyl acrylate and *N*-*n*-octadecylacrylamide, side-chain crystallinity developing at higher ester or amide compositions eventually raised the glass transition. The behavior of *n*-octadecyl acrylate and methyl methacrylate copolymers was previously illustrated.²³ There it was shown that T_g began to rise slowly, starting at a weight fraction in C_{18} -side-chain ester of about 0.4. This was the composition at which crystallinity first appeared. The behavior of copolymers of *N*-*n*-octadecylacrylamide with methyl methacrylate is illustrated in Figure 1. The dashed line represents the decline in T_g with increasing weight fraction of amide w_b and its subsequent rise beyond w_b of 0.4. The dotted line represents the melting of side-chain crystallinity; the lower part of the curve represents the onset of melting, the upper where melting is complete. In contrast to the *n*-octadecyl acrylate copolymers,²³ the present vitreous transitions all occurred above the melting transition. In addition, the scanning-peak breadths, taken as measures of crystallite-size distributions,²⁷ were much greater than for copolymers containing the long-chain ester. The numbers in the figure correspond to the notation of reference 23. Also, the decline of the heat of fusion with decrease in amide was somewhat greater than with *n*-octadecyl acrylate.²² This would be the behavior expected of

TABLE II
Composition, Glass Transition Temperature, Flex Temperature, and Mechanical Properties of Copolymers^a

Long-side-chain comonomer ^b		Glass and flex temperatures		Flexural properties		Tensile properties		
Mole fraction	Weight fraction	T_g , °C	T_f , °C	Strength, psi	Modulus, psi $\times 10^{-6}$	Strength, psi	Modulus, psi $\times 10^{-5}$	Elongation, %
<i>n</i> -Butyl acrylate and methyl methacrylate								
0	0	101.6	82.3	4578	1.96	7762	2.20	5.0
0.050	0.063	101.0	83.0	4950	2.10	7880	2.00	5.0
0.075	0.094	89.3	91.0	5020	2.04	9140	1.91	7.0
0.100	0.125	81.7	77.0	4480	1.99	8340	1.76	8.0
0.125	0.155	81.0	75.0	4650	2.06	9180	1.69	7.0
0.150	0.184	76.0	75.0	4530	2.04	7880	1.64	6.0
0.200	0.243	65.7	65.0	4330	2.01	8350	1.53	7.0
0.300	0.354	48.0	47.0	3520	1.64	6670	1.44	9.0
0.400	0.461	30.0	21.0	1360	0.587	4340 ^c	0.889	120.0
0.500	0.561	15.0	-7.0	65	0.028	1190 ^c	0.189	275.0
0.600	0.658	0.3	-46.0	—	—	347 ^c	0.0079	425.0
0.750	0.793	-20.7	—	—	—	—	—	—
2-Ethylhexyl acrylate and methyl methacrylate								
0.050	0.088	92.0	73.0	3860	1.67	8000	1.66	6.0
0.075	0.130	84.0	60.0	3410	1.54	6540	1.45	6.0
0.100	0.170	79.0	61.0	3210	1.50	7110	1.45	6.0
0.125	0.208	72.0	58.0	3080	1.36	4675	1.38	4.0
0.150	0.245	67.0	53.5	2940	1.36	7100	1.52	8.0
0.200	0.315	56.0	41.0	2120	0.988	6100	1.18	10.0
0.300	0.441	37.0	-6.0	681.0	0.316	1850	0.256	65.0
0.400	0.551	22.0	-32.0	321.0	0.052	545	0.0403	173.0
0.500	0.648	3.0	-48.0	—	—	85	0.0013	425.0
0.600	0.734	-11.0	—	—	—	—	—	—
0.750	0.847	-26.0	—	—	—	—	—	—

n-Octadecyl acrylate and methyl methacrylate

0.050	0.146	77.0	60.0	3700	1.56	5125	1.77	3.0
0.075	0.208	57.8	53.0	3075	1.39	6800	1.46	10.0
0.100	0.265	38.0	40.0	2300	1.07	5125	1.23	7.0
0.125	0.317	39.0	32.0	1700	0.789	4050	1.17	6.0
0.150	0.364	26.0	22.0	1350	0.630	3400	0.986	23.0
0.200	0.448	17.0	2.0	700	0.337	2250	0.461	30.0
0.300	0.582	22.0	-22.0	285	0.138	1275	0.255	260.0
0.400	0.683	20.7	-30.0	270	0.137	1275	0.255	95.0
0.500	0.764	20.7	-30.0	500	0.249	1725	0.343	5.0
0.600	0.829	17.0	-40.0	630	0.320	750	0.338	2.0
0.750	0.907	21.0	-85.0	980	0.493	335	0.398	1.0

Oleyl acrylate and methyl methacrylate

0.050	0.145	73.6	58.0	2400	1.25	4100	1.98	1.0
0.075	0.207	61.3	47.0	2060	1.32	6390	1.26	10.0
0.100	0.264	50.3	36.0	1560	0.933	5040	1.07	10.0
0.125	0.315	21.7	15.0	1000	0.588	3550	0.457	20.0
0.150	0.362	26.0	-2.0	540	0.313	2570	0.149	40.0
0.200	0.446	5.0	-29.0	140	0.0755	1740	0.0761	70.0
0.300	0.580	-14.3	-75.0	—	—	330	0.0111	75.0
0.400	0.682	-42.3	-79.0	—	—	100	0.0006	115.0
0.500	0.763	-49.0	—	—	—	—	—	—
0.600	0.829	-57.0	—	—	—	—	—	—
0.750	0.906	-45.0	—	—	—	—	—	—

(continued)

TABLE II (Continued)

Long-side-chain comonomer ^b		Glass and flex temperatures		Flexural properties		Tensile properties		
Mole fraction	Weight fraction	T_g , °C	T_f , °C	Strength, psi	Modulus, psi $\times 10^{-5}$	Strength, psi	Modulus, psi $\times 10^{-5}$	Elongation, %
<i>N</i> - <i>n</i> -Butylacrylamide and methyl methacrylate								
0.050	0.063	97.0	84.0	4475	2.03	7550	1.99	7.0
0.075	0.094	96.3	90.0	4500	1.99	8025	1.75	8.0
0.100	0.124	94.3	66.0	4450	1.95	7275	1.59	6.0
0.125	0.154	93.0	68.0	4275	1.94	8225	1.62	8.0
0.150	0.183	90.6	58.0	4275	1.94	5925	1.65	4.0
0.200	0.241	91.0	65.0	4200	1.92	4175	1.84	2.0
0.300	0.353	86.6	53.0	4025	1.75	3425	2.00	2.0
0.400	0.459	75.5	52.0	3400	1.57	3350	1.92	2.0
0.500	0.560	81.3	49.0	3075	1.42	3550	1.33	3.0
0.600	0.656	83.6	46.0	2950	1.32	2675	1.86	2.0
0.750	0.792	85.6	39.0	2625	1.07	2150	1.26	2.0
<i>N</i> - <i>n</i> -Octylacrylamide and methyl methacrylate								
0.050	0.088	93.6	85.0	4725	2.19	7075	1.79	5.0
0.075	0.129	87.3	84.0	4525	2.06	8200	1.79	7.0
0.100	0.169	85.3	80.0	4750	2.09	8500	1.74	7.0
0.125	0.207	79.0	77.0	4525	2.00	6200	1.64	5.0
0.150	0.244	65.3	51.0	3650	1.56	2775	1.42	2.0
0.200	0.314	60.3	49.0	3200	1.46	2275	1.46	2.0
0.300	0.440	46.0	45.0	2525	1.16	2900	1.32	3.0
0.500	0.647	35.0	15.0	1500	0.700	2100	1.03	2.0
0.600	0.733	36.3	-25.0	1250	0.590	2500	0.620	5.0
0.750	0.846	37.0	-78.0	875	0.410	2275	0.570	7.0
<i>N</i> - <i>n</i> -Octadecylacrylamide and methyl methacrylate								
0.050	0.145	84.6	63.0	3475	1.57	5350	1.62	4.0
0.075	0.208	72.0	55.0	3225	1.44	3025	1.34	2.0
0.100	0.264	65.0	48.0	2850	1.31	3375	1.44	3.0
0.125	0.316	42.5	44.0	2475	1.14	2500	1.34	2.0

0.150	0.363	44.0	39.0	2250	1.05	2150	1.07	2.0
0.200	0.447	46.0	5.0	1350	0.600	600	0.750	1.0
0.300	0.581	50.0	-33.0	1225	0.570	600	0.560	1.0
0.400	0.683	54.5	-39.0	1150	0.530	200	0.260	1.0
0.500	0.764	51.7	-43.0	1200	0.560	225	0.280	1.0
0.600	0.829	69.7	-24.0	1525	0.660	225	0.300	1.0
0.750	0.907	72.3	-38.0	1850	0.840	—	—	—
<i>N</i> - <i>n</i> -Oleylacylamide and methyl methacrylate								
0.050	0.145		70.0	3475	1.53	3800	1.79	3.0
0.075	0.207	87.0	60.0	2960	1.39	4290	1.51	4.0
0.100	0.263	68.0	52.0	2585	1.10	3350	1.13	3.0
0.125	0.315		47.0	2045	0.867	3670	1.07	4.0
0.150	0.362	55.0	41.0	1630	0.729	3490	0.975	3.0
0.200	0.445	45.0	25.0	1085	0.492	2470	0.763	5.0
0.300	0.579		-33.0	545	0.236	2030 ^e	0.334	33.0
0.400	0.682		-64.0	340	0.139	1475 ^e	0.189	60.0
0.500	0.763	-13.0	-68.0	180	0.0803	1130 ^e	0.139	100.0
0.600	0.828		-78.0	110	0.0498	870 ^e	0.0939	115.0
0.750	0.906	-43.0	-85.0	75	0.0346	665 ^e	0.0634	25.0
Vinyl stearate and methyl methacrylate ^d								
0.024	0.0702	109.0	85.0	4450	1.83	6580	1.93	5.0
0.036	0.104	89.0	68.0	3750	1.64	7400	1.64	6.0
0.046	0.129	88.0	70.0	3840	1.68	5740	1.63	4.0
0.076	0.203	86.0	50.0	3140	1.44	2430	1.69	1.5
0.158	0.368	—	40.0	2425	1.10	1430	1.31	1.0
0.183	0.410	82.0	37.0	1570	0.738			
0.197	0.433	79.0	18.0	1480	0.757			
0.377	0.622	77.0	-44.0	910	0.466			
0.414	0.687	—	10.0	980	0.467			
0.375	0.650	72.0	-35.0	850	0.437			
0.744	0.899	—	—	410	0.214			
0.902	0.966	75.0	—	320	0.160			
0.950	0.983	—	—	200	0.102			

TABLE II (Continued)

Long-side-chain comonomer ^b		Glass and flex temperatures		Flexural properties		Tensile properties		
Mole fraction	Weight fraction	T_g , °C	T_f , °C	Strength, psi	Modulus, psi $\times 10^{-5}$	Strength, psi	Modulus, psi $\times 10^{-5}$	Elongation, %
<i>n</i> -Octadecyl acrylate and ethyl acrylate and methyl methacrylate								
0	0.250 ^e	49.7	45.0	3185	1.47	5910	1.23	6.0
0.050 ^f	0.326 ^e	37.7	44.5	2660	1.14	4010	1.03	4.5
0.100 ^f	0.387 ^e	19.5	20.0	1310	0.619	3090	0.627	16.0
0.150 ^f	0.439 ^e	18.5	9.0	975	0.466	2050	0.428	11.5
0.200 ^f	0.482 ^e	9.5	-3.0	750	0.347	1570	0.301	13.0
0	0.500 ^e	10.6	6.0	132	0.053	1230	0.0129 ^g	120.0
0.050 ^h	0.550 ^e	-2.4	-4.0	31.8	0.012	895	0.0075 ^g	315.0
0.100 ^h	0.592 ^e	-8.5	-16.0	17.4	0.007	615	0.0052 ^g	225.0
0.150 ^h	0.626 ^e	-5.5	-20.0	19.7	0.009	370	0.0028 ^g	485.0
0.200 ^h	0.655 ^e	-8.0	-26.0	11.9	0.006	431	0.0034 ^g	360.0
0.250 ^h	0.680 ^e	-7.0	-32.0	20.2	0.009	583	0.0052 ^g	235.0

^a Yields were 85-98%; mostly 95%. Midrange of the vinyl stearate copolymers was 39-67%.

^b In feed. Compositions by elemental analysis agreed with these within experimental error.

^c Yield strength.

^d Compositions calculated from elemental analysis.

^e Sum of weight fractions of *n*-octadecyl acrylate and ethyl acrylate.

^f Ethyl acrylate, mole fraction: 0.25, 0.20, 0.15, 0.10, 0.05; methyl methacrylate, mole fraction: 0.75, all samples.

^g 100% modulus.

^h Ethyl acrylate mole fraction: 0.50, 0.45, 0.40, 0.35, 0.30, 0.25; methyl methacrylate; mole fraction: 0.50, all samples.

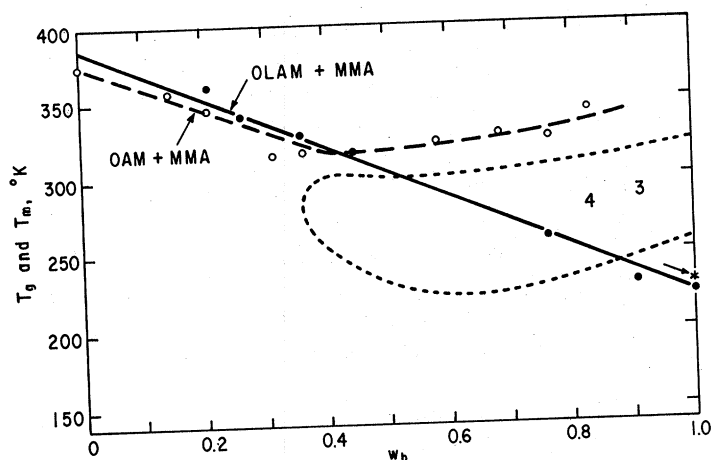


Fig. 1. Plots of the glass transition temperature T_g and the melting temperature T_m vs. the weight fraction w_b of long-side-chain ester for copolymers of, respectively, *N-n*-octadecylacrylamide and *N*-oleylacrylamide. The dotted line defines the melting range of the octadecylacrylamide copolymers.

copolymers whose crystallinity develops in aggregates of side chains, which are distributed as a dispersed phase in a stiff glassy matrix. In contrast, the greater conformational freedom allowed the acrylate copolymers, by their lower T_g , permitted more crystallinity of better perfection to develop.^{22,23}

The solid line in Figure 1 represents the decline in T_g for the completely amorphous *N*-oleylacrylamide-methyl methacrylate copolymer. The slope of this curve and that for the *N-n*-octadecylacrylamide copolymers are the same in the composition region before crystallinity commences in the latter system. On extrapolation, the two curves reached limiting values (star and solid circle in the figure) close to an average T_g of -48.0°C for the homopolymers. This is higher than the average value of -111°C for the C_{18} acrylate ester homopolymer, found by extrapolating T_g data for random copolymers of *n*-octadecyl acrylate or oleyl acrylate and several comonomers.²³ It appears that the glass transitions of 18 carbon polyacrylamides are sensitive to their functional structure. This is an exception to the conclusion reached from the extrapolation of T_g , T_f , or brittle temperature data for the homopolymers of lower homologs having a variety of structures, to a chain length of 18 carbon atoms.¹⁸ From the data collected in this paper the glass transitions of poly-*N-n*-butyl- and poly-*N-n*-octylacrylamide are, respectively, 59.2°C and 11.7°C .

Relationship between the Mechanical Properties and Composition

The data of Table II relating the mechanical properties to the weight fraction w_b of the long-side-chain esters or amides were fitted by computer in accordance with the equation

$$A = A_0 + Bw_b + B'w_b^2 + \dots \quad (1)$$

where A is the mechanical property of the copolymer, A_0 is the same property for the poly(methyl methacrylate) used in this work, and B, B' etc. are the coefficients corresponding to different degrees in w_b . The analysis of variance revealed that first degree polynomials were the most significant for the compositions in the glassy region. The parameters are listed in Table III. Specific designation of the parameters, expressed in general form in eq. (1), are: E_f , flex modulus; FS, flex strength; E_t , tensile modulus; TS, tensile strength. Values of B are designated $\alpha, \beta, \gamma, \delta$ for the properties in the order given above. Trends for the slopes ($\alpha, \beta, \gamma, \delta$) were similar. They generally increased as the side-chain length decreased. The slopes for the esters were greater than those for the corresponding amides.

In a number of cases, moduli and strengths fell to very small values at w_b considerably less than unity, which is the value of w_b for the homopolymer. Moreover, the rapid decline of properties occurred when most of the copolymers were still in their glassy state at room temperature. While it is true that lowering the glass temperature is equivalent to raising the test temperature with T_g constant, because moduli and tensile strengths always decrease with increase in temperature,²⁸⁻³⁰ the magnitude of these effects seemed excessive. Furthermore, raising temperature should produce yield strengths less than brittle strengths,^{26,30} because the potential for deformation instability is minimized. This was not observed. The observations can possibly be explained after first considering the relation of the glass temperature to composition.

Contribution of Chain-End Plasticization to the Glass Transition

The general empirical equation relating the monotonic lowering of the glass transition to the diluent concentration, for either external or internal plasticization, is^{31,32}

$$T_g = T_{g,a}w_a + T_{g,b}w_b + Kw_aw_b \quad (2)$$

where $T_{g,a}$ and $T_{g,b}$ are the glass transition temperatures of the base polymer and plasticizer, respectively, w_a and w_b are their respective weight fractions, and K is an empirical constant which, for externally plasticized systems, has values between 58 and -300°K .³² Equation (2) could be applied to the data in Table II because the decline in T_g was monotonic for all amorphous copolymer compositions, a situation not always encountered in copolymers.^{33,34} In special cases, where $K = 0$, eq. (2) simplifies to

$$T_g = w_aT_{g,a} + w_bT_{g,b} \quad (3)$$

Here the decline in T_g with composition is linear, so that

$$T_g = T_{g,a} - kw_b \quad (4)$$

where $T_{g,a} > T_{g,b}$ and $k = T_{g,a} - T_{g,b}$. Throughout this paper the subscript a refers to methyl methacrylate while the subscript b refers to the higher n -alkyl acrylates, N - n -alkylacrylamides or vinyl ester, respectively.

TABLE III
Curve-Fitting Parameters for the Mechanical Properties Described by Equation (1)

Copolymer system ^a	Flexural modulus ^b		Flexural strength ^b		Tensile modulus ^b		Tensile strength ^b	
	$E_f \times 10^{-5}$, psi	$\alpha \times 10^{-5}$, psi	$FS_0 \times 10^{-4}$, psi	$\beta \times 10^{-4}$, psi	$E_{t,0} \times 10^{-5}$, psi	$\gamma \times 10^{-5}$, psi	$TS_0 \times 10^{-4}$, psi	$\delta \times 10^{-4}$, psi
BA + MMA	2.11	-0.882	0.503	-0.344	2.14	-2.52	0.956	-1.26
EHA + MMA	2.05	-3.59	0.460	-0.803	2.09	-3.48	0.770	-1.25
OA + MMA	2.05	-3.80	0.478	-0.919	2.22	-3.51	0.789	-1.17
OLA + MMA	2.00	-4.34	0.421	-0.987	2.40	-5.54	0.793	-1.26
BAM + MMA	2.11	-1.21	0.472	-0.267	1.93	-0.567	0.733	-0.742
OCAM + MMA	2.26	-2.27	0.510	-0.523	2.03	-1.76	0.742	-0.714
OAM + MMA	2.01	-2.86	0.459	-0.686	2.08	-2.72	0.581	-0.823
OLAM + MMA	1.95	-3.15	0.461	-0.800	2.17	-3.26	0.585	-0.634
VS + MMA	1.81	-1.90	0.416	-0.449	2.04	-2.13	0.803	-1.92
OA + EA + MMA	2.07	-3.35	0.496	-0.887	2.25	-4.14	0.813	-1.29
Average	2.04		0.468		2.14		0.757	

^a Data from Table II not included in the correlation were: BA + MMA, w_b 0.46-0.66 for E_f and FS, w_b 0.56-0.66 for E_t ; OA + MMA, w_b 0.58-0.91 for E_f and FS, w_b 0.58-0.91 for E_t and FS, w_b 0.59-0.68 for E_f and FS, w_b 0.76-0.91 for E_t ; OLAM + MMA, w_b 0.68-0.91 for E_f and FS, w_b 0.55-0.68 for E_t and FS. The same averages for the

^b Average deviations taken as the 95% confidence limits were, for the intercepts; moduli ± 0.09 ; strength ± 0.04 . The same averages for the slopes were $\alpha \pm 0.24$, $\beta \pm 0.10$, $\gamma \pm 0.29$, $\delta \pm 0.15$.

The glass transition-composition data in Table II all followed eq. (4) as long as the systems remained amorphous. The constants $T_{g,a}$ and k for the amorphous copolymers are listed in Table IV. Because the average value of K [eq. (2)] for a variety of external plasticizers is about -150°K ,³² as compared to 0° for internal plasticizers, the present results suggest that internal plasticizers will be less efficient than externals in lowering the glass transition of a stiff homopolymer.

The contributions of segmental motion to fractional free volume of polymers in the glass transition region have been treated by many.³⁵ Tobolsky³² concluded that a monomeric diluent increased free volume by effectively lowering the molecular weight of a plasticized system through the proliferation of chain ends introduced by the plasticizer. Boyer⁹ had reached a similar conclusion much earlier. As Tobolsky suggested, these principles can also be applied to internally plasticized copolymers, such as those of this paper. The relations of Tobolsky³² will now be modified so that this can be accomplished.

The equation relating glass transition temperature to molecular weight³⁶ is

$$T_g = T_{g,a} - c/\bar{M}_n \quad (5)$$

where $T_{g,a}$ is the glass transition temperature of a polymer of "infinite" molecular weight, having essentially no chain ends. If each plasticizing co-unit in the present internally plasticized systems is considered to introduce a chain end through the pendent side chain, the number-average molecular weight of the plasticized system, $\bar{M}_{n,c}$, becomes

$$\bar{M}_{n,c} = 1/(w_a/\bar{M}_n + w_b/M_{0,b}) \quad (6)$$

where \bar{M}_n is the number-average molecular weight of the copolymer and is the source of the chain ends contributed by the main polymer chain, while $M_{0,b}$ is the formula weight of the internal plasticizer co-unit. The latter contribute chain ends through the side groups. Modification of eq. (5) in the light of eq. (6) yields

$$T_g = T_{g,a} - c_p(w_a/\bar{M}_n + w_b/M_{0,b}) \quad (7)$$

where the subscript p denotes the plasticized system. Because the contribution of w_a/\bar{M}_n is insignificant compared to $w_b/M_{0,b}$ in lowering the molecular weight in eq. (6), except at very large w_a , eq. (7) simplifies to

$$T_g = T_{g,a} - c_p w_b/M_{0,b} \quad (8)$$

Since $c_p = kM_{0,b}$, eq. (8) reduces to eq. (4). Values of c_p for all of the copolymer systems are listed in Table IV. Values of c_p increased as the side chains of the b co-units became longer in both the n -alkyl acrylate and the N - n -alkylacrylamide copolymers. Plots of c_p versus the number n of methylene groups in the side chains reveal (Fig. 2) that the change in c_p with n is similar for the two sets of copolymers. Consequently, the contribution

TABLE IV
Parameters for the Relation of Glass Transition Temperature to Composition and Ratios of Mechanical Property to Glass
Transition Correlation Constants

Parameters for the Relation of Glass Transition Correlation Constants								
Copolymer system	Glass transition, °K ^a		k	$-\alpha/k$ $\times 10^{-3}$	$-\beta/k$	$-\gamma/k$ $\times 10^{-3}$	$-\delta/k$	$c_p \times 10^{-4}$
	T_g	T_{g^a}						
BA + MMA	377.9 ± 1.1	159.9 ± 2.6	0.552 ^b	21.51 ^b	1.576	78.80	2.05	
EHA + MMA	380.8 ± 3.1	167.4 ± 6.1	2.145	47.97	2.079	74.67	3.09	
OA + MMA	375.9 ± 4.5	213.4 ± 18.2	1.781	43.06	1.645	54.83	6.93	
OLA + MMA	374.6 ± 4.0	210.0 ± 10.2	2.067	47.00	2.638 ^b	60.00	6.77	
BAM + MMA	372.9 ± 1.4	40.58 ± 5.0	2.982	65.80	1.397	182.8 ^b	0.516	
OCAM + MMA	368.1 ± 4.1	83.31 ± 9.3	2.725	62.78	2.113	85.70	1.53	
OAM + MMA	374.3 ± 6.2	144.7 ± 21.7	1.977	47.41	1.880	56.88	4.68	
OLAM + MMA	385.3 ± 4.9	164.7 ± 9.5	1.913	48.57	1.979	38.49	5.20	
VS + MMA	370.0 ± 3.5	30.82 ± 7.6	6.165 ^b	145.7 ^b	6.911 ^b	622.9 ^b	0.957	
OA + EA + MMA	371.1 ± 3.1	183.2 ± 7.2	1.829	48.42	2.260	70.41	1.83	
Average	375.1		2.180	51.40	1.870	65.00		
							BAM + MMA, w_b 0.66-0.91, MMA w_b 0.76-0.91, OA + MMA w_b 0.66-0.91	

^a Data from Table II not included in the correlation were: OA + MMA, w_b 0.45-0.91; OLA + MMA, w_b 0.76-0.91; BAM + MMA, w_b 0.66-0.79; OAM + MMA, w_b 0.58-0.91; OA + EA + MMA, w_b 0.63-0.68.

^b Not included in the average values.

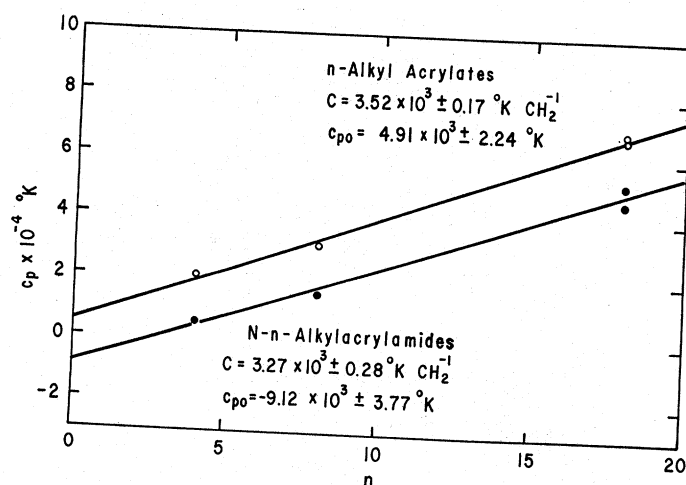


Fig. 2. Plots of c_p of eq. (8) vs. the number of methylene groups in the side chain.

of each methylene group in lowering T_g is additive. The relationship, therefore, is

$$c_p = c_{p,0} + C(n) \quad (9)$$

where $c_{p,0}$ is a parameter characterizing the relative stiffness of the internal plasticizer as part of the main chain. The smaller algebraically $c_{p,0}$ is, the less efficient a given plasticizing structure with linear side-chains will be, compared to others having similar alkyl groups. Values of $c_{p,0}$ and C for the two systems are given in the figure.

It might be instructive to consider the molecular contribution to fractional free volume of the constant c of eq. (5) and c_p in eq. (8). The free volume per cubic centimeter contributed by the chain ends of homopolymers, ϕ , is related^{35,37} to c by

$$c = 2\rho N\phi/\alpha' \quad (10)$$

where ρ is the density of the homopolymer, N is Avogadro's number, and α' is the difference between the expansion coefficients of the liquid and glassy polymers, respectively. This difference for many polymers is close to $4.8 \times 10^{-4} \text{cm}^3/\text{g-deg}$. The constant 2 indicates that each chain contributes two chain ends. In the copolymers of this investigation, where each side chain contributes only one chain end, the relation becomes

$$c_p = \rho N\phi/\alpha' \quad (11)$$

Because each methylene group donates a constant unit of free volume, in view of eq. (9), the free volume associated with each CH_2 group is given, eq. (12), in \AA^3 , by differentiating eq. (9), after substituting $\rho N\phi/\alpha'$ for c_p .

$$d\phi/dn = \Delta\phi_n = C/[\rho N(1/\alpha')] \quad (12)$$

In employing eq. (12) to estimate $\Delta\phi_n$, the quantity ρ for each CH_2 was taken as 0.8712 g/cm^3 , with a literature molar volume³⁸ of $16.1 \text{ cm}^3/\text{mole}$. The average value of $2.45 \times 10^{-4} \text{ cm}^3/\text{g-deg}$, given by Rogers and Mandelkern³⁹ for the poly(*n*-alkyl methacrylate) homopolymers, was taken for α' . The free volume for each methylene group was calculated to be $1.6 \text{ \AA}^3/\text{CH}_2$ for the *n*-alkyl acrylates and $1.5 \text{ \AA}^3/\text{CH}_2$ for the *N*-*n*-alkylacrylamides. Since these values are within 40% of the volume of a single methylene group, they are of the correct magnitude.³⁷ The observations here are in harmony with the additive contributions to free volume made by each methylene group in a homologous series, through regular changes in their specific volumes³⁹ and their relaxation spectra,^{40,41} with change in *n*. These experimental facts are usually attributed to a regular decrease in the frictional coefficient, ζ_0 , with increasing side-chain lengths,^{13b} after reduction to a reference temperature. Because ζ_0 is sensitive to the functional structure of the co-unit,^{13b} larger values of the coefficient at a common reference temperature, for any given side-chain length, should be found for the *N*-*n*-alkylacrylamides than were found for the esters. The amides are indeed less efficient plasticizers, since $c_{p,0}$ is algebraically smaller in this series. It remains now to consider the relation of *C* and $c_{p,0}$ to mechanical properties.

Relation between the Glass Transition Temperature and Mechanical Properties

Boyer⁹ observed that the plasticized polystyrenes, when tested in the vitreous state, had tensile strengths which were linear functions of their heat-distortion temperatures, which he used as equivalent to T_g . Ratios of the slopes *B* (or $\alpha, \beta, \gamma, \delta$) of eq. (1) to *k* [eq. (4)] were likewise roughly constant in this work, as can be seen in columns 4, 5, 6, 7 of Table IV. Average values (with the omissions specified) are also given in the table. These average constants permit the calculation of the mechanical properties by eq. (13) using the parameters taken from Figure 2, the average values of A_0 of eq. (1) (Table III, average values), and the ratios *B/k* given as average values in columns 4, 5, 6, 7 of Table IV. Equation (13) results from combining eqs. (1), (4), and (9). Thus, for tensile modulus, E_t

$$E_t = E_{t,0} + (\gamma/k)[(c_{p,0} + Cn)/M_{0,b}]w_b \quad (13)$$

Equation (13) only applies to the composition region in which the glass transition temperature is above room temperature. It was observed from some of the data in this work, and from consideration of data in other plasticized systems,^{3,14} that the change of the slope *B* with composition increases roughly 10 times at test temperatures above T_g . This observation permitted a term to be added to eq. (13) to account for the change in mechanical properties through the transition region. With the term added, eq. (13) becomes

$$E_t = E_{t,0} + (\gamma/k)[(c_{p,0} + Cn)/M_{0,b}]w_b - (10\gamma)w_b^{S_0 - an} \quad (14)$$

where S_0 and a are empirical constants. Solution in the computer by an iterative procedure yielded, for the n -alkyl acrylates $S_0 = 14$, $a = -0.5$; for the N - n -alkylacrylamides, $S_0 = 64.0$, $a = -3.0$. All of the mechanical properties for all of the copolymers listed in Table II were calculated by using eq. (14). The tensile modulus data, typical of the rest, are given in Figure 3 as the lines (solid and dashed) in the figure, with the experimental points being added. Agreement is fairly good, considering the nature of the equation, the approximations made in arriving at the last term, and the experimental scatter. The equation failed completely in estimating the following data: the flexural moduli and strength for the n -butyl acrylate copolymers and the flexural strengths of the N - n -butylacrylamide copolymers. In addition, the badly scattered experimental tensile strengths were but poorly predicted. Of course, the equation was never intended for use with the crystalline copolymer compositions. In general, however, eq. (14), besides being convenient for yielding smoothed data, illustrates

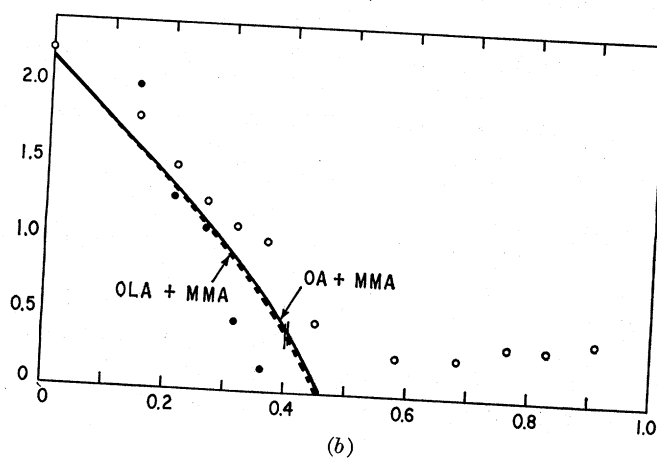
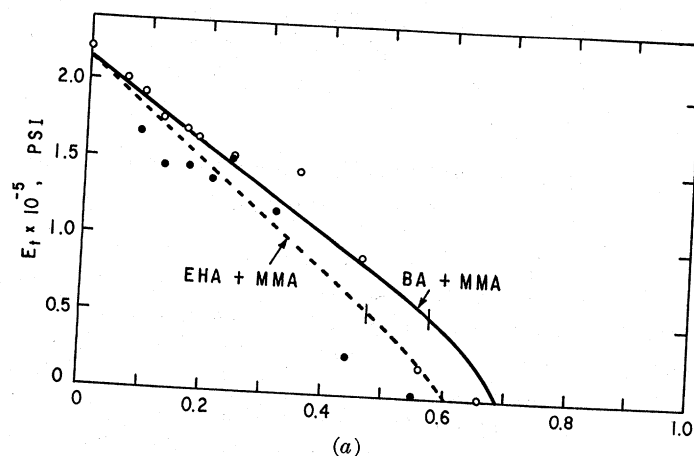


Fig. 3. (continued)

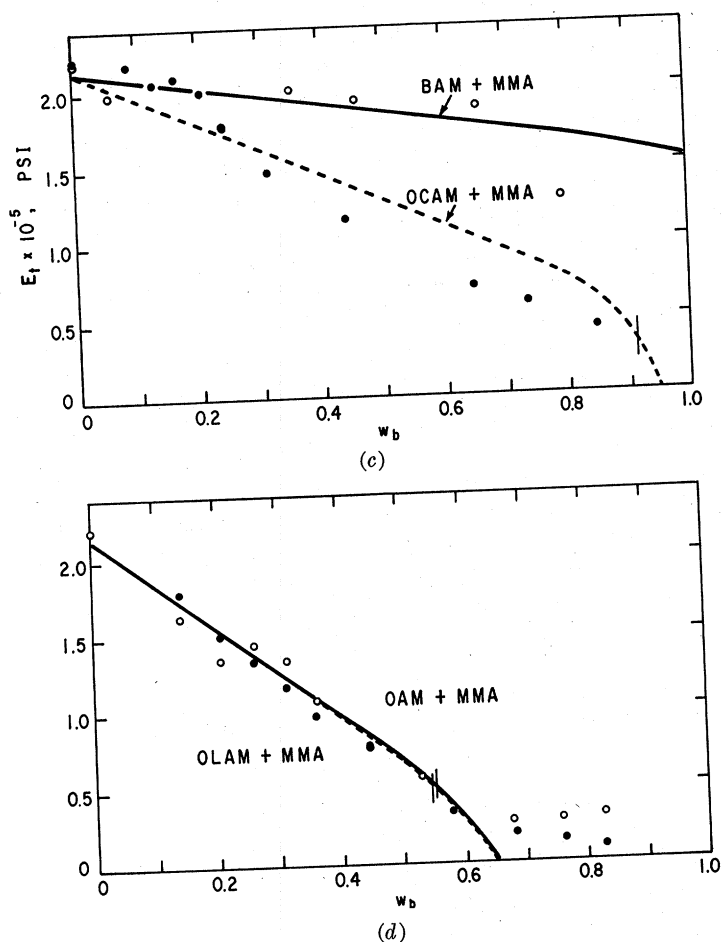


Fig. 3. Plots of tensile modulus vs. the weight fraction of fatty acrylate ester or acrylamide: (a) experimental data for the copolymers of (O) *n*-butyl acrylate (BA) and (●) 2-ethylhexyl acrylate (EHA) with methyl methacrylate (MMA); (b) experimental data for copolymers of (O) *n*-octadecyl acrylate (OA), and (●) oleyl acrylate (OLA) with methyl methacrylate; (c) experimental data for copolymers (O) of *N*-*n*-butylacrylamide (BAM) and (●) *N*-*n*-octylacrylamide (OCAM) with methyl methacrylate; (d) experimental data for (O) *N*-*n*-octadecylacrylamide (OAM) and (●) *N*-oleylacrylamides (OLAM) with methyl methacrylate. Vertical lines denote compositions where the testing temperature corresponded to the glass transition temperature. Lines are calculated from eq. (14).

the strong dependency of the mechanical properties of these copolymers on the additive contribution to free volume made by each methylene group. It further demonstrates that the efficiency of chain-end plasticization in copolymers³² depends on additivity in side-chain length as well as on the functional structure of the plasticizing comonomer.

The probable origin of the fracture properties of these systems should be considered briefly. It was noted above that all samples showed brittle

fracture at compositions at which T_g was above room temperature, but demonstrated significant strain, with irreversible flow, only when T_g was below this temperature. In the amorphous copolymers, this behavior may be caused by stress concentration,²⁶ having its source in aggregations of side chains, insoluble in the main chains, which are formed in the polymer matrix.¹⁸ The deformation energy would tend to concentrate at the boundaries of these regions, which act as microvoids and thus propagate fracture. The data here illustrate the disordering effect in the matrix exerted by a proliferation of chain ends and its effect in eliminating the relaxation times associated with the rubbery region of the relaxation spectrum. It is these relaxation times that are responsible for the desirable inelastic contributions to fracture.²⁶ The problem is aggravated when side-chain crystallinity is present. The large spherulites then formed act even more effectively to produce micro voids.⁴² In externally plasticized crystalline polymers the restraining crystal network,^{5,11,12} dispersed throughout the liquid matrix, furnishes the rubbery relaxation times eliminated in amorphous systems.¹² Externally plasticized amorphous compositions seem to have particularly poor properties. When the data of Boyer⁹ for amorphous polystyrene were analyzed by the methods of this paper, δ was 2 to 4 times greater than found for the copolymers studied here, while k was of similar magnitude.

Terpolymers, Nonrandom Copolymers, and Correlation of T_g with T_f and T_d

It has been seen that eqs. (9) and (14) accurately estimate the glass transition temperatures and mechanical properties for the amorphous copolymers via an additive contribution of each methylene group to free volume. Consequently, terpolymers, consisting of two homologs of different side-chain lengths and methyl methacrylate, should also obey eq. (9). To test this, terpolymers were prepared having different combinations of *n*-octadecyl and ethyl acrylate with methyl methacrylate. Calculated values of T_g are compared in Table V with found values. Information necessary to the calculation is given in Table V and in footnotes of Table II. Agreement is good enough to illustrate the general utility of eq. (9), although the T_g for the ethyl acrylate-methyl methacrylate copolymers do not agree closely with the found values.

In a previous publication²³ it was suggested that in nonrandom copolymers, like vinyl stearate and methyl methacrylate, heterophase aggregation characterized the decline in the glass transition with increasing vinyl ester. Consequently the value of k (Table IV) was small and the melting points of the side chains of vinyl stearate²² were scarcely depressed. The effect of excessive phase separation is also reflected in the mechanical properties (Table II). Anomalous values of the mechanical property parameters of Tables III and IV further emphasize this behavior. It may be concluded that in nonrandom copolymers long-side-chain co-units are poor plasticizers.

TABLE V
Glass Transition Temperatures of the Terpolymers Calculated by
Using the Parameters of Figure 2 Compared with
Experimental Values

w_b^a	n^b	$c_p \times 10^{-4}$	Glass transition, °K	
			Calculated	Found
0.250	2.0	1.19	341.3	322.8
0.326	9.16	3.71	310.8	310.8
0.387	12.9	5.04	294.1	292.6
0.439	15.3	5.86	281.3	291.6
0.482	16.9	6.42	270.8	282.6
0.500	2.0	1.91	311.5	283.7
0.550	6.24	2.68	278.5	270.7
0.592	9.16	3.71	261.6	264.6
0.626	11.3	4.47	249.9	256.4 ^c
0.655	12.9	5.04	241.0	251.1 ^c
0.680	14.2	5.49	233.6	246.7 ^c

^a $w_b = w_b' + w_b''$, where w_b is weight fraction and prime denotes ethyl acrylate, double prime denotes *n*-octadecyl acrylate.

^b $n = (w_b'/w_b) 2.0 + (w_b''/w_b) 18.0$.

^c Calculated by using eq. (4) to obtain values undistorted by crystallinity.

The Clash-Berg flex temperature is often taken as being close to the glass transition, T_g .^{18,19} Another temperature of importance is the T_4 temperature. It lies close to the inflection temperature T_i of typical modulus-temperature curves.¹⁹ Values of T_g were plotted as a function of both T_i and T_4 . The quantities T_g and T_i are from Table II; T_4 values are not listed. Values of T_i for all of the copolymers in Table II, except the butylacrylamide and vinyl stearate systems, were correlatable; for T_4 the *N*-*n*-octadecylacrylamide system was also eliminated. Correlations were linear and slopes were 0.798 ± 0.038 for T_i and 0.998 ± 0.032 for T_4 . Intercepts were 78.4 ± 9.5 for T_i and -13.2 ± 10.8 for T_4 . Because the theoretical slope of unity and zero intercept were approached, T_g correlated remarkably well with T_4 for the abundant data collected here.

SUMMARY AND CONCLUSIONS

Mechanical properties were correlated with glass transitions for selected copolymers of higher *n*-alkyl acrylates or *N*-alkylacrylamides with methyl methacrylate. The complete range of compositions was investigated. It was concluded that the decrease in tensile and flexural moduli and strengths with increase in fatty component was proportional to the decrease in T_g . The additive contribution to free volume by each side-chain methylene group was responsible for this behavior. Side chains attached to the copolymer backbone by amide links were less efficient plasticizers, however, than those attached by ester links, since the amide function restricted conformational freedom of main chains to a greater extent. An empirical equation was developed describing the decrease of the mechanical property

parameters with composition for the amorphous copolymers through the transition region, where the rate of decline increased. All samples showed brittle fracture, except those tested in the transition region, where flow often characterized the strain. Side-chain crystallization interfered only slightly with the mechanical properties, because moduli and strengths had already fallen to small values near compositions where crystallinity commenced. Nonrandom copolymers of vinyl stearate and methyl methacrylate were not effectively plasticized, because heterogeneity caused phase separation.

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Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

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